Energy, Mines and Resources Canada | Énergie, Mines et Ressources Canada

CANMET

Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

THE PARTITIONING OF IMPURITIES DURING LEAD ELECTROWINNING FROM MOLTEN CHLORIDE ELECTROLYTE

D.J. MacKinnon, J.M. Brannen and J.M. Skeaff
Extractive Metallurgy Laboratory

December 1982

Project MRP-3.4.0.0.02
Hydrometallurgical Lead Process

This document is an unedited interim report prepared for discussion and information purposes. It does not represent a final evaluation of the opinion of the Canada Centre for Mineral and Energy Technology (CANMET)

Ce document est un rapport [illegible] rédigé [illegible] de communication [illegible] nullement [illegible] définitive de [illegible] canadien de la technologie des minéraux et de l'énergie (CANMET)

22 pp

MINERALS RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES
DIVISION REPORT MRP/MSL 82-135 (TR)

THE PARTITIONING OF IMPURITIES DURING LEAD ELECTROWINNING FROM MOLTEN CHLORIDE ELECTROLYTE

by

D.J. MacKinnon*, J.M. Brannen** and J.M. Skeaff*

ABSTRACT

The partitioning of the impurities Ag, Cu, Fe and Bi between electrowon lead and the molten salt electrolyte has been determined at 500°C for the ternary electrolyte $PbCl_2$-NaCl-KCl. Most of the Ag reported to the lead bullion but virtually all of the Fe remained in the electrolyte. About 25% of the Cu reported to the lead metal and the amount of Bi in the bullions increased with increasing Bi concentrations in the electrolyte. Silver and Bi had no effect on the current efficiency but both Cu and Fe caused a significant decrease in the current efficiency for lead deposition.

---

* Research Scientist and ** Research Technician, Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources Canada, 555 Booth Street, Ottawa, Ontario K1A 0G1.

INTRODUCTION

Existing and proposed regulations to control the lead smelter work place environment have led to an extensive study of novel extraction techniques to replace the present sinter/blast furnace method for lead production. Hydrometallurgists have focussed their attention on chloride-based leach/electrolysis processes (1-3). CANMET has also adopted the chloride route as the basis for its Hydrometallurgical Lead Process which is being developed for treating Canadian lead concentrates containing silver values and deleterious impurities, and also for treating the lead residues produced by processes designed to extract metal values from complex sulphide bulk concentrates.

Chloride process for lead will result in a $PbCl_2$ product which could be advantageously processed by fused salt electrolysis to recover the lead and regenerate chlorine gas for recycle. Sulphate processes will result in a $PbSO_4$ product which could be converted readily to $PbCl_2$ by brine leaching. A major technical hurdle to overcome in this process is the electrolysis step. The literature on the fused salt electrolysis of lead and other chlorides was reviewed recently (4). The review indicated that bench-scale or pilot-scale studies on fused salt electrolysis of lead chloride using both monopolar and bipolar cells have established a range of operating conditions that yield current efficiencies >95%. The tests which yielded the highest current efficiencies were those in which the electrolyte was free of both oxides and water, and the electrolysis was conducted at temperatures as low as possible consistent with maintaining both electrolyte and metal in the molten state.

Although some success has already been achieved with the fused salt electrolysis of lead chloride, more work is required to resolve the problems associated with heat balances, electrode configurations, feeding and removal systems, electrolyte composition, etc. Another area which requires further attention is the effect of electrolyte impurities on the purity of the lead bullion. According to the standard electromotive series, Ag, As, Bi, Cu, Fe and Sb all have lower standard decomposition potentials than Pb and could co-deposit with the lead. Sodium, Sn and Zn have higher decomposition potentials than Pb and should not be found in the metal as long as the $PbCl_2$ concentration is relatively high. Haver et al. (5) found that while all the Ag and Sb in a LiCl-KCl-$PbCl_2$ molten salt bath deposited with the Pb, most of the Cu and Fe remained in solution.

The present study was undertaken to determine the partitioning of Ag, Cu, Fe and Bi between the NaCl-KCl-$PbCl_2$ molten salt melt and the bullion during the fused salt electrolysis of lead chlorides.

EXPERIMENTAL

ELECTROLYSIS CELL AND ELECTRODES

The electrolysis cell, electrode assembly and resistance furnace are shown schematically in Figure 1. The cell consisted of a 45-mm diameter Vycor tube, 25-cm long, sealed at the bottom. This tube contained the molten Pb cathode (75 g) and the molten NaCl-KCl-$PbCl_2$ electrolyte. The Vycor tube was placed inside a 60-mm diameter Pyrex tube, 30-cm long, which in turn was placed in the heating chamber of a resistance furnace. The outer Pyrex tube was sealed at the bottom and fitted with a Teflon stopper at the top. The electrodes, as well as an inlet tube for N_2 or HCl gas and a gas outlet, passed through the Teflon stopper into the inner Vycor tube.

Electrical contact to the molten Pb cathode was via a glass-shielded graphite rod; the reference probe, also graphite, dipped into the molten $PbCl_2$ electrolyte, and was positioned near the lead cathode. The purpose of the probe was to provide a measure of the cathode potential during electrolysis. The anode was also constructed from graphite and was placed in the $PbCl_2$ electrolyte above the molten Pb cathode.

ELECTROLYTE COMPOSITION AND PREPARATION

The electrolyte consisted of 0.6 mole fraction $PbCl_2$ + 0.2 mole fraction NaCl and 0.2 mole fraction KCl. This particular composition is well within the thermodynamically calculated (6) range of one-phase liquid solution and was also calculated to have a vapour pressure of 13.3 Pa; i.e., low enough that significant melt volatilization should not occur. Thus the standard electrolyte consisted of 176.7 g $PbCl_2$ + 11.6 g NaCl + 14.8 g KCl for a total weight of 203 g. All materials were dried at 130°C and stored in a dessicator. Increments of $PbCl_2$ weighing 20.8 g were also prepared for addition to the cell on an hourly basis.

The effect of the impurities Ag, Cu, Fe and Bi was studied by adding their respective chlorides to the electrolyte. The amount of impurity added varied between 0.1 and 1.0 wt % of the electrolyte. The same percentage of the respective impurities was also incorporated in the $PbCl_2$ increments added on an hourly basis.

EXPERIMENTAL PROCEDURE

The charge consisting of 203 g of electrolyte + 75 g Pb metal (cathode) was placed in the cell and heated to 500°C under N_2 for 0.5 h. The molten system was then treated with HCl gas for 1 h to try to eliminate water.

Following the HCl treatment, electrolysis was begun and lasted from 6 to 18 hours under an N_2 atmosphere. The Cl_2 produced at the anode was absorbed in a 50 g/L NaOH solution.

Current to the cell was provided at constant voltage; the cathode potential was recorded and the total coulombs passed during electrolysis was measured using an Ampere-hour meter. A constant voltage of 4 V was imposed across the anode and cathode that resulted in a current of approximately 4 A. Across about 1-h of electrolysis the current began to decrease and at this point a fresh increment of $PbCl_2$, containing sufficient Pb to replace that which had been deposited, was added to the cell. Upon addition of the $PbCl_2$ increment, the current increased to $\sim$4 A.

After the prescribed electrolysis time, 6, 12 or 18 h, the Teflon top was removed from the cell, and the melt was poured into a crucible and cooled. After cooling, the Pb metal and the final salt electrolyte were separated. The lead metal was analysed by emission spectroscopy to determine low levels of impurities; higher impurity concentrations were determined by chemical analysis. The fused salt electrolyte was also analyzed.

RESULTS AND DISCUSSION

CURRENT EFFICIENCY

The effect of the impurities AgCl, $CuCl_2$, $FeCl_2$ and $BiCl_3$ on the current efficiency of lead electrowinning from molten chloride electrolyte was studied over a range of concentrations varying from 0.1 to 1.0 wt % of the electrolyte. The results are shown in Figure 2 as a plot of current efficiency vs per cent added impurity. These results, which were obtained for a 6-h electrolysis period, indicate that AgCl and $BiCl_3$ had no effect

on the current efficiency for lead electrowinning. Increasing concentrations of either $CuCl_2$ or $FeCl_3$ resulted in a significant reduction in the current efficiency for lead electrowinning, from >98% for no impurity addition to about 82% for 0.8 wt % impurity addition. This reduction in current efficiency may be attributed to the cyclic oxidation-reduction of Cu and Fe ions.

The effect of the impurities AgCl, $CuCl_2$ and $BiCl_3$ on the current efficiency for lead electrowinning as a function of electrolysis time is shown in Figure 3 for 0.5 % impurity addition. The current efficiency remained unchanged over the 18-h electrolysis period when 0.5 wt % AgCl was added to the electrolyte, but decreased rapidly with increasing electrolysis time when 0.5 wt % $CuCl_2$ or 0.5 wt % $FeCl_2$ were present in the electrolyte.

IMPURITY DISTRIBUTION

Effect of Impurity Concentration

The distribution or partitioning of Ag, Cu, Fe and Bi between the electrowon Pb and the molten electrolyte was determined as a function of the impurity concentration of the electrolyte for a 6-h electrolysis period. The results are summarized in Tables 1-4 in terms of weight of impurity contained in the electrowon lead and in the electrolyte. In the case of Ag (Table 1) most of this impurity reports to the electrowon lead. For 0.1 and 0.3 wt % AgCl, the total Ag analysed and the amount added to the system were within 9%. For the larger additions of AgCl, i.e., 0.5 and 0.8 wt %, there was a discrepancy of 16-19% between the total Ag analysed and the amount added to the system. The minimum amount of Ag reporting to the bullion was 0.08%, which is four times the ASTM specification for chemical lead (7).

The results obtained for $CuCl_2$ additions (Table 2) indicate that about 25% of the Cu reported to the bullion and that 75% remained in the electrolyte. In this case, excellent agreement was obtained between the total Cu analysed and the amount added to the system. This result is in good agreement with the data obtained by Haver et al. (5) for the corresponding LiCl-KCl-$PbCl_2$ system. The minimum amount of Cu reporting to the electrowon lead was 0.12% which is 50% greater than the ASTM specification for chemical lead (7).

The data shown in Table 3 indicate that almost all of the Fe added to the system remained in the electrolyte, although the lowest Fe content of the lead exceeded the ASTM specifications by almost a factor of 10. Again a good balance between total Fe analysed and Fe added to the system was obtained. In the case of Bi, the data shown in Table 4 indicate that the amount of the impurity reporting to the electrowon lead increases with increasing additions to the system. The total Bi analysed was in good agreement with the amount added to the electrolyte. As with Fe, the minimum amount of Bi in the bullion exceeded with ASTM specification by a factor of 10.

Effect of Electrolysis Time

The effect of electrolysis time on the distribution of Ag, Cu and Fe between the electrowon Pb and the molten salt electrolyte was determined for the electrolytes containing 0.5 wt % of one of AgCl, $CuCl_2$ and $FeCl_2$. The data are summarized in Tables 5-7 inclusive. These results indicate that most of the Ag reports to the electrowon Pb (Table 5) with the amount appearing to increase with increasing electrolysis times. The agreement between the total Ag analysed and Ag added to the system was generally poor. The amount of Cu reporting to the electrowon Pb

increased with increasing electrolysis time as indicated by the data in Table 6. Almost all of the Fe remains in the molten electrolyte (Table 7). Excellent agreement (<7%) between the total metals analyzed and the metals added was obtained for the $CuCl_2$ and $FeCl_2$ systems (Tables 6 and 7).

CONCLUSIONS

The effect of AgCl, $CuCl_2$, $FeCl_2$ and $BiCl_3$ on the current efficiency for lead electrowinning from molten $PbCl_2$-NaCl-KCl electrolyte has been determined. AgCl and $BiCl_3$ in concentrations up to 0.8 wt % of the electrolyte had no effect on the current efficiency whereas $CuCl_2$ and $FeCl_2$ resulted in significant decreases in the current efficiency.

The partitioning of Ag, Cu, Fe and Bi between the electrowon lead and the molten salt electrolyte has also been determined. Most of the Ag reported to the lead metal, but most of the Fe remained in the electrolyte. About 25% of the Cu reported to the bullion over a 6-h electrolysis period, regardless of the copper concentration in the electrolyte. For longer electrolysis times, the amount of copper reporting to the lead metal increased becoming 44% after 18 h. The amount of Bi reporting to the bullion increased with increasing Bi concentrations in the electrolyte. Impurity accountability was good except for silver where significant variations were noted between metal added and that analyzed.

Metal chloride impurities in the chloride melt invariably reported to the electrowon lead in amounts greater than ASTM specifications. It is thus evident that each impurity in the $PbCl_2$ melt used for electrolysis must be significantly less than 0.1%.

ACKNOWLEDGEMENTS

Thanks are due to R.E. Horton for the spectrochemical analysis of the lead metal and to J.C. Hole and D.J. Barkley for chemical analysis of the lead metal and electrolyte.

REFERENCES

1 - Wong, M.M., Haver, F.P. and Sandberg, R.G. "Ferric chloride leach-electrolysis process for production of lead"; LEAD-ZINC-TIN '80; edited by J.M. Cigan, T.A. Mackey and T.J. O'Keefe; TMS-AIME, Warrendale, Pennsylvania; 445-454; 1979.

2 - Demarthe, J.M. and Georgeaux, A. "Hydrometallurgical treatment of lead concentrate"; LEAD-ZINC-TIN '80; edited by J.M. Cigan, T.A. Mackey and T.J. O'Keefe; TMS-AIME, Warrendale, Pennsylvania; 426-444; 1979.

3 - Stauter, J.C., Tolley, N.K. and Um, R.T. "The recovery of lead from sulphide concentrates using a chlorination/brine leach/electrolysis process"; ACS Meeting; Anaheim, California; March 1978.

4 - Skeaff, J.M. "The electrowinning of aluminum, magnesium, lead and zinc from molten chloride electrolytes: A survey"; Trans Inst Min and Metal 88:C71-82; 1980.

5 - Haver, F.P., Engles, C.H., Bixby, D.L. and Wong, M.M. "Recovery of lead from lead chloride by fused salt electrolysis"; USBM RI 8166; 18; 1976.

6 - Skeaff, J.M., Bale, C.W., Pelton, A.D. and Thompson, W.T. "Calculated thermodynamic properties of ternary fused chloride systems for the electrowinning of lead and zinc"; Division Report MRP/MSL 79-23; CANMET, Energy, Mines and Resources Canada; 1979.

7 - "Metals Handbook: Ninth Edition"; Metals Park, Ohio, U.S.A., American Society for Metals; 1979.

Table 1. Partitioning of Silver Between Electron Lead and Molten Electrolyte

AgCl	Ag	ASTM spec*	Silver Distribution						
				In Pb^{o}		In Electrolyte		Total Ag	Analyzed
(%)	(G)	(%)	wt (%)	(G)	(%)	(G)	(%)	(G)	(% input)
0.1	0.25	≤0.02	0.08	0.18	75.0	0.06	25.0	0.24	96
0.3	0.74		0.75	0.72	89.8	0.09	11.2	0.81	109.5
0.5	1.23		1.9	1.41	94.6	0.08	5.4	1.49	121.1
0.8	1.98		1.9	1.69	95.8	0.07	4.2	1.67	84.3

Electrolysis time: 6 hr

* for chemical lead

Table 2. Partitioning of Copper Between Electrowon Lead and Molten Electrolyte

Copper Added			Copper Distribution						
			In Pb^o			In Electrolyte		Total Cu	Analyzed
$CuCl_2$ (%)	Cu (G)	ASTM spec* (%)	wt (%)	(G)	distr (%)	(G)	(%)	(G)	(% input)
0.3	0.47	≤0.08	0.12	0.11	26.2	0.31	73.8	0.42	89.4
0.5	0.78		0.28	0.19	23.8	0.61	76.2	0.80	102.5
0.8	1.20		0.38	0.31	25.2	0.92	74.8	1.23	102.5

Electrolysis time: 6 h

* for chemical lead

Table 3. Partitioning of Iron Between Electrowon Lead and Molten Electrolyte

Iron Added			Iron Distribution						
			In Pb^o			In Electrolyte		Total Fe	Analyzed
$FeCl_2$ (%)	Fe (G)	ASTM spec* (%)	wt (%)	(G)	distr. (%)	(G)	(%)	(G)	(% input)
0.1	0.14	≤0.002	0.028	0.02	12.5	0.14	87.5	0.16	114.3
0.3	0.44		0.021	0.02	4.8	0.40	95.2	0.42	95.5
0.5	0.73		0.026	0.02	2.9	0.68	97.1	0.70	95.9
1.0	1.44		0.028	0.02	1.5	1.34	98.5	1.36	94.4

Electrolysis time: 6 hr

*for chemical lead

Table 4. Partitioning of Bismuth Between Electrowon Lead and Molten Electrolyte

$BiCl_3$	Bi	ASTM spec*	Bismuth Distribution						
			In Pb^o			In Electrolyte		Total Bi	Analyzed
(%)	(G)	(%)	wt (%)	(G)	(%)	(G)	(%)	(G)	(% input)
0.1	0.21	≤0.005	0.048	0.042	15.6	0.23	84.4	0.27	128.5
0.3	0.65		0.11	0.103	14.5	0.61	85.9	0.71	109.2
0.8	1.74		0.74	0.66	38.2	1.07	61.8	1.73	99.4

Electrolysis time: 6 hr

* for chemical lead

Table 5. The Effect of Electrolysis Time on Silver Distribution between Electrowon Pb and Molten Electrolyte

Time	Ag Added	Silver Distribution In Pb^{o}		In Electrolyte		Total Ag	Analyzed
(H)	(G)	(G)	(%)	(G)	(%)	(G)	(% Input)
6	1.23	1.41	94.6	0.08	5.4	1.49	121.1
12	1.70	1.29	96.3	0.05	3.7	1.34	78.8
18	2.21	2.36	99.2	0.02	0.8	2.38	107.7

0.5% AgCl Added to Electrolyte

Table 6. The Effect of Electrolysis Time on Copper Distribution Between Electrowon Pb and Molten Electrolyte

Time	Cu Added	Copper Distribution In Pb^{o}		In Electrolyte		Total Cu	Analyzed
(H)	(G)	(G)	(%)	(G)	(%)	(G)	(% Input)
6	0.78	0.19	23.8	0.61	76.3	0.80	102.6
12	1.08	0.35	31.8	0.75	68.2	1.10	101.9
18	1.38	0.60	44.4	0.75	55.6	1.35	97.8

0.5% $CuCl_2$ Added To Electrolyte

Table 7. The Effect of Electrolysis Time on Iron Distribution Between Electrowon Pb and Molten Electrolyte

		Iron Distribution					
Time	Fe Added	In Pb^{o}		In Electrolyte		Total Fe	Analyzed
(H)	(G)	(G)	(%)	(G)	(%)	(G)	(% Input)
6	0.73	0.02	2.9	0.68	97.1	0.70	95.9
12	1.00	<0.002	<0.2	0.93	100.0	0.93	93.0
18	1.28	<0.002	<0.1	1.25	100.0	1.25	97.7

0.5% $FeCl_2$ Added to Electrolyte

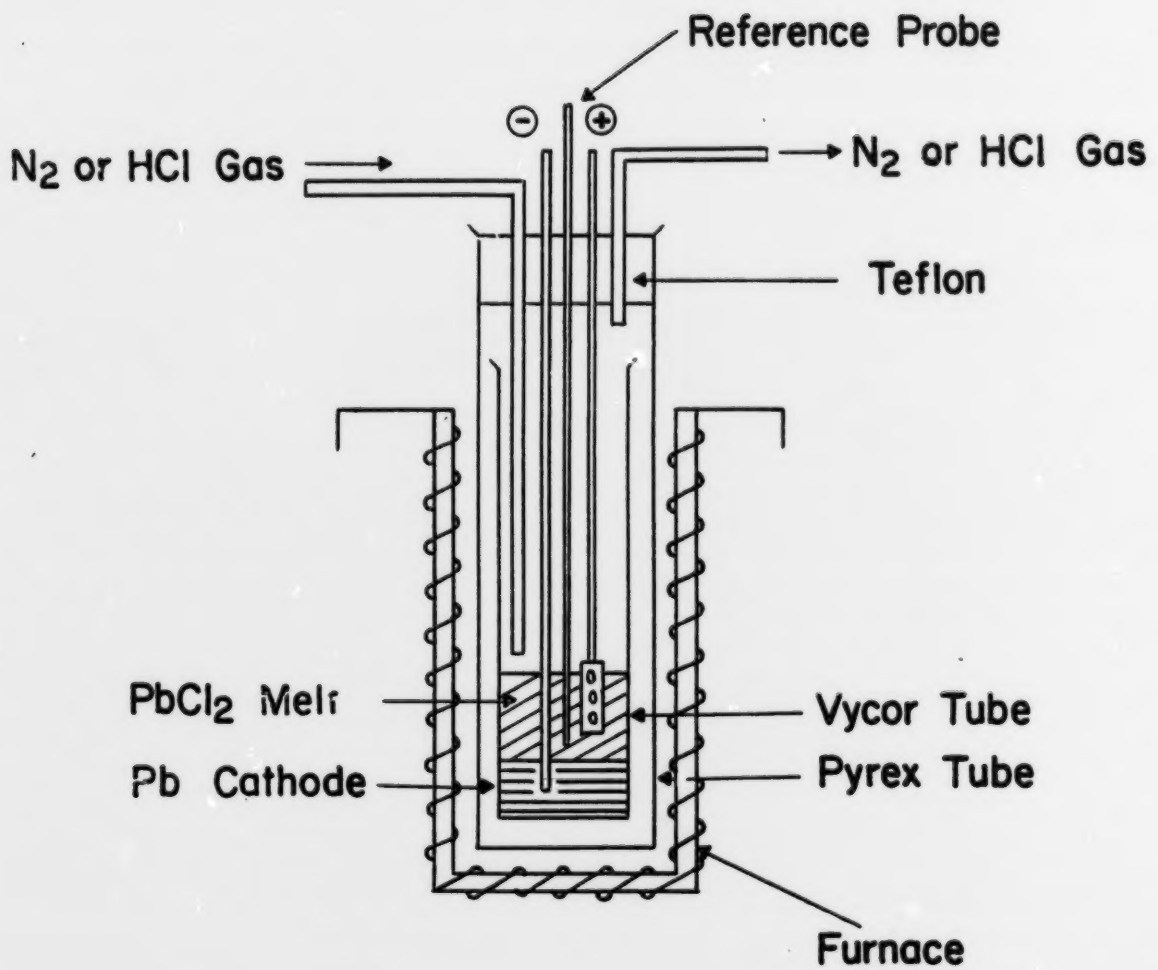
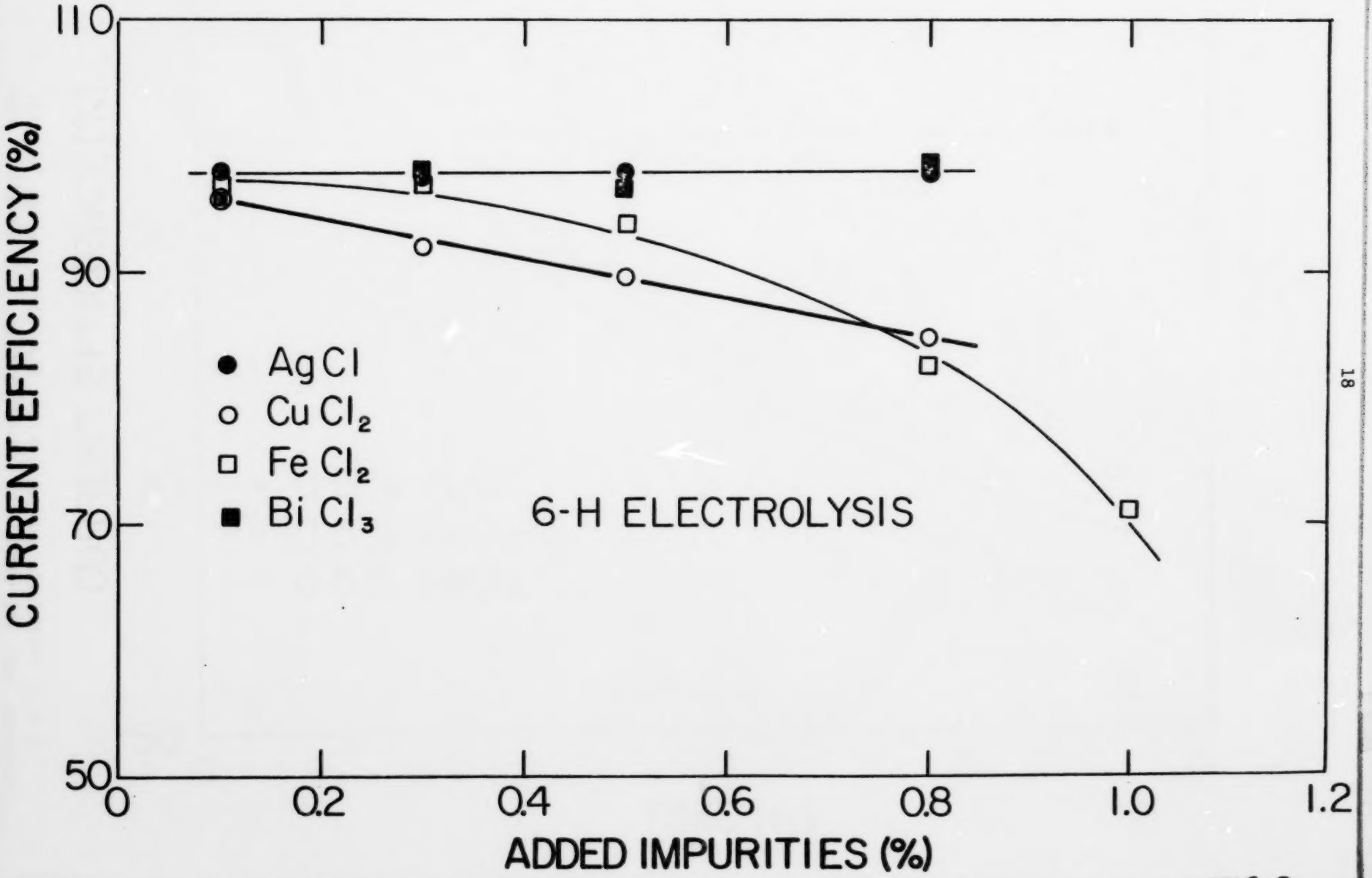


Fig. 1 - Schematic drawing of the fused salt electrolysis cell

FIG. 1

Fig. 2 - Plots of current efficiency vs added impurities showing the effect of Ag, Cu, Fe and Bi on the current efficiency for lead deposition over a 6-h electrolysis period



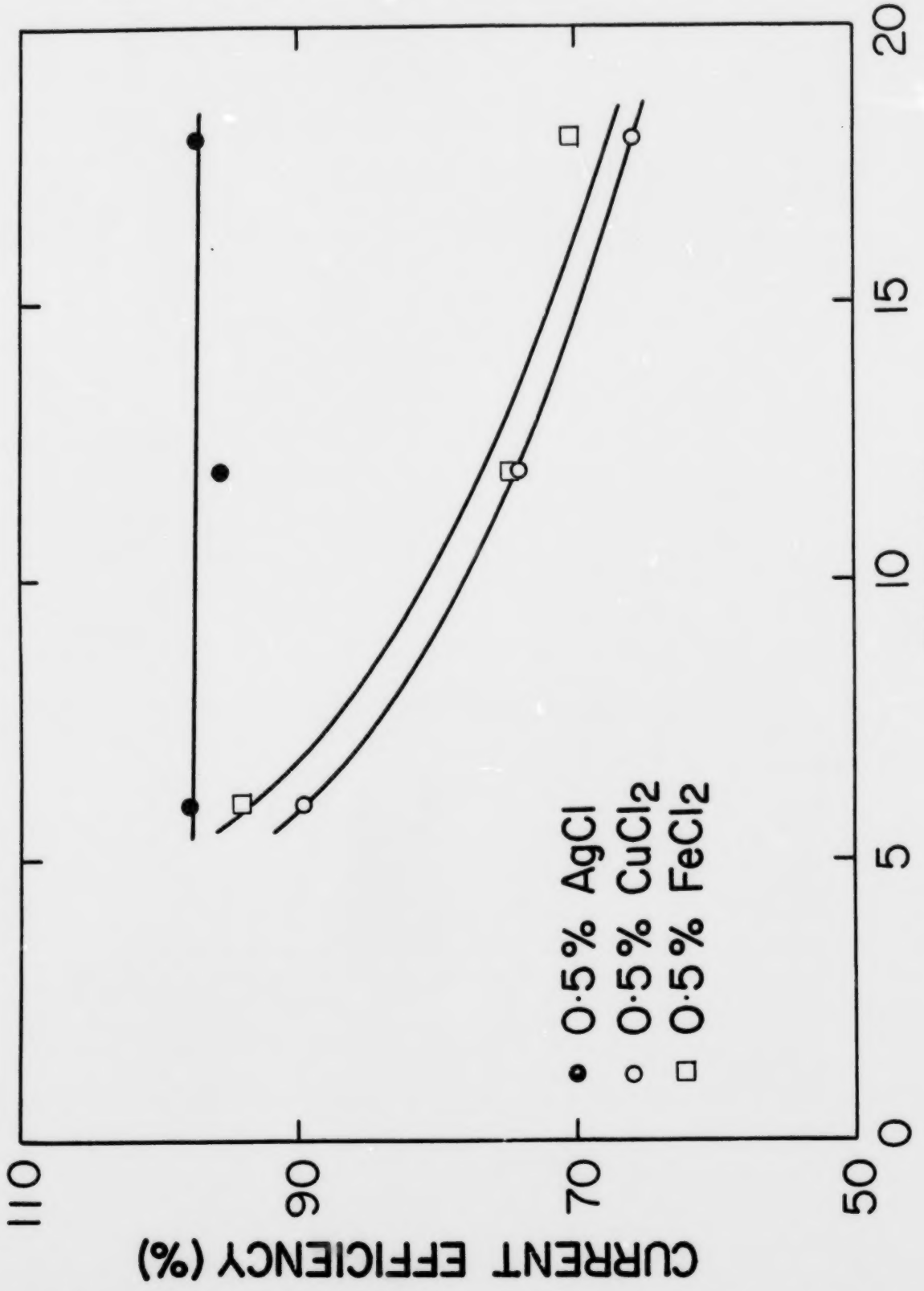


FIG. 3

Fig. 3 - Plots of current efficiency vs time showing the effect of 0.5% AgCl, $CuCl_2$ and $FeCl_2$ on the current efficiency for lead deposition